

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification<sup>4</sup> :

H01J 40/00, 47/00, B05D 5/12

A1

(11) International Publication Number:

WO 87/07762

(43) International Publication Date:

17 December 1987 (17.12.87)

(21) International Application Number: PCT/US87/01364

(22) International Filing Date: 4 June 1987 (04.06.87)

(31) Priority Application Number: 870,437

(32) Priority Date: 4 June 1986 (04.06.86)

(33) Priority Country: US

(71) Applicant: LAZARUS, Steven [US/US]; University of Chicago, 1101 East 58th Street, Chicago, IL 60637 (US).

(72) Inventors: YOUNG, Charles, E. ; 65 West 59th Street, IG, Westmont, IL 60559 (US). PELLIN, Michael, J. ; 25 West 259 Salem, Naperville, IL 60540 (US). GRUEN, Dieter, M. ; 1324 59th Street, Downers Grove, IL 60515 (US).

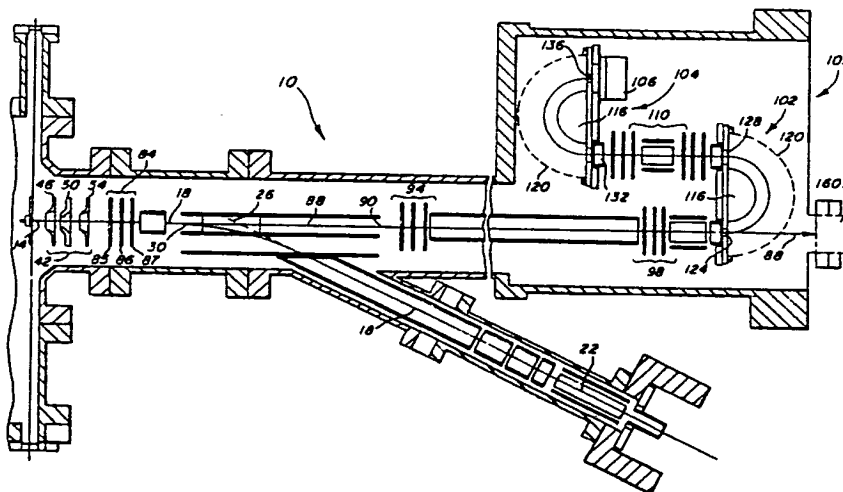
(74) Agent: RECHTIN, Michael, D.; Niro, Scavone, Haller &amp; Niro, Ltd., 200 West Madison - Suite 3500, Chicago, IL 60606 (US).

(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).

Published

With international search report.

(54) Title: PHOTO ION SPECTROMETER



(57) Abstract

A method and apparatus for extracting for quantitative analysis ions of selected atomic components of a sample (14). A lens system (46, 50, 54) is configured to provide a slowly diminishing field region for a volume containing the selected atomic components, enabling accurate energy analysis of ions generated in the slowly diminishing field region. The lens system (46, 50, 54) also enables focusing on a sample (14) of a charged particle beam, such as an ion beam (18), along a path length perpendicular to the sample and extraction of the charged particles (88) along a path length also perpendicular to the sample (14). Improvement of signal to noise ratio is achieved by laser excitation of ions to selected autoionization states before carrying out quantitative analysis. Accurate energy analysis of energetic charged particles is assured by using a preselected resistive thick film configuration disposed on an insulator substrate for generating predetermined electric field boundary conditions to achieve for analysis the required field potential. The spectrometer also is applicable in the fields of SIMS, ISS and electron spectroscopy.

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

- 1 -

## PHOTO ION SPECTROMETER

Contractual Origin of the Invention

The U. S. Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the U. S. Department of Energy and Argonne National Laboratory.

Background of the Invention

The present invention relates generally to a charged particle spectrometer. More particularly the invention relates to an ion spectrometer having a lens system configured to extract from a sample ionized atomic components having well controlled energy and also to provide precise spatial manipulation of the various ion beams, enabling highly sensitive detection of the ionized atomic components. Improvement of signal to noise ratio is also achieved by exciting the atomic components to autoionization states before performing energy and angular refocusing time of flight (hereinafter, "EARTOF") mass spectrometric analysis.

Significant advances have been made in the quantitative analysis of atomic components in a sample. For example, resonance ion spectrometers have demonstrated considerable sensitivity for the detection of atoms of a predetermined component. (See, for example, USPN 4,442,354 and 3,987,302 (Hurst et al.) and U. S. Patent Application Serial No. 691,825, which are incorporated by reference herein). In practice, however, these previous resonance ion spectrometers still have significant limitations in terms of achieving sensitivities in the part per trillion range because of severe difficulties encountered in discriminating low level signals to be measured from noise made up of competing, undesired and extraneous signals.

O b j e c t s

It is therefore an object of the invention to provide an improved spectrometer for quantitative analysis of selected atomic components.

- 2 -

It is another object of the invention to provide a novel ion spectrometer wherein a predetermined electric field is applied to ions enabling improved detection sensitivity of selected atomic components from a sample.

It is an additional object of the invention to provide an improved resonance ion and an autoionization spectrometer wherein a pulsed electric field is applied to a sample for repelling unwanted ions prior to extraction of photo ions generated by laser beam pulse excitation of selected atomic components.

It is another object of the invention to provide an improved spectrometer lens system having appropriately shaped lens structures for minimizing the redeposition probability of unwanted impurities from the lens system onto a sample.

It is an additional object of the invention to provide a novel spectrometer lens system enabling both the focusing of a primary ion beam along a path perpendicular to a sample and extraction of ions from a sample along a path also perpendicular to the sample and leading to a detector at the end of the spectrometer.

It is a further object of the invention to provide an improved device for generating predetermined electric field boundary conditions to achieve a required electric field potential for the desired use, such as the EARTOF analysis.

It is another object of the invention to provide a mass spectrometer construction having two complementary electrostatic analyzers with spherical electrical fields and an interposed telescopic lens for analyzing charged particle beams, such as the ionized selected atomic components.

A significant feature in accordance with the instant invention lies in the provision of an improved spectrometer having enhanced sensitivity for detecting selected atomic components of a sample. A lens system is configured to provide a predetermined slowly diminishing electric field region for a volume containing a large portion of the ionized

- 3 -

form of the selected atomic components, thereby minimizing the energy spread of the volume of the ionized selected atomic components which are subsequently extracted for spectroscopic analysis, such as in an EARTOF spectrometer. The relatively small energy spread makes the spectroscopic analysis substantially more accurate and increases the signal to noise ratio. In another aspect of the invention, the lens system also applies a pulsed electric field to the sample to remove some of the unwanted secondary ions from the volume containing neutral ones of the selected atomic components prior to their ionization. The pulsed electric field also places some of the unwanted secondary ions into high energy escape orbits, causing the secondary ions to be rejected in subsequent stages of the spectrometer 10. Once the unwanted ions are removed from the volume, the selected atomic components are excited to an ionized state, including selected autoionization states which provide enhanced discrimination of unwanted ionized species.

In an additional aspect of the invention, the lens system is adapted to perform a number of different spatial manipulations of various charged particle beams. For example, the lens system can guide a primary ion beam perpendicular to the surface of the sample, while also adapted for extracting ions of the selected atomic component perpendicular to the sample surface along a path leading to the detector at the end of the spectrometer.

In a further aspect of the invention, the final stages of the lens system include two complementary spherical electric field sections. A preselected resistive thick film configuration is disposed on an insulator substrate for generating predetermined electric field boundary conditions for any one of a number of uses. In particular, the resistive thick film configuration is used in conjunction with the spherical electrostatic analyzers,

- 4 -

achieving the required electric field potential necessary for accurate EARTOF spectrometer analysis and minimization of signal loss.

Further objects and advantages of the present invention, together with the organization and manner of operation thereof, will become apparent from the following detailed description of the invention when taken in conjunction with the accompanying drawings wherein like reference numerals designate like elements in the several views.

#### Brief Description of the Drawings

FIGURE 1 illustrates an ion spectrometer constructed in accordance with one embodiment of the invention;

FIGURE 2 shows a fragmentary view of the sample chamber and ion extraction region of the spectrometer of FIG. 1;

FIGURE 3 illustrates a predetermined electric field as a function of perpendicular distance from the sample area shown in FIG. 2;

FIGURE 4 is an enlarged fragmentary view of the sample area during generation of ions for analysis;

FIGURE 5 illustrates a timing cycle for generation of an ionized beam of the selected atomic component;

FIGURE 6A depicts the orbits in the electrostatic analyzer of ions having various energies and FIG. 6B illustrates the orbits of ions entering at different angles with the same energy;

FIGURE 7 shows a plan view of an example of the components of a preselected thick film configuration on an insulator substrate.

#### Detailed Description of the Preferred Embodiment

Referring now to the drawings, and in particular to FIGS. 1 and 2, an improved ion spectrometer constructed in accordance with one embodiment of the present invention

- 5 -

is indicated at 10. Very generally, the ion spectrometer 10 (hereinafter, the "spectrometer 10") includes a sample 14 disposed within a high vacuum (less than about  $10^{-9}$  Torr.) provided by a conventional ultra high vacuum pumping system (not shown). Measurement of the quantity of a selected atomic component from the sample 14 is carried out by removing atoms for subsequent quantitative analysis. The selected atomic component is removed from the sample 14 by irradiating the sample 14 with an energetic particle beam, such as an ionized particle beam 18 (hereinafter, "primary ion beam 18") in the illustrated embodiment. A substantial portion of the selected atomic component removed from the sample 14 originates from a sample region 15, shown in FIG. 4, wherein the flux is highest from the primary ion beam 18. Typically, inert gas ions are used as the primary ion beam 18 and have an energy of 5kV. The primary ion beam 18 is preferably a pulsed beam (see FIG. 5) in order to cooperate with other physical events (some of which are shown in FIG. 5), enabling performance of various functionalities to be described hereinafter. The primary ion beam 18 is deflected by deflector plates 22 from a first path 26 to a second path 30, which intersects the sample 14 substantially perpendicular thereto. In other forms of the invention the energetic particle beam can be other types of beams, such as, for example, a neutral particle beam, an electron beam, fission fragments or a photon beam, such as a laser beam. When the primary ion beam 18 strikes the sample 14, various atoms, including the selected atomic component, are ejected from the sample 14. A volume containing a number of the selected atomic component is therefore generated near the sample 14.

In order to remove unwanted ions from the volume containing the selected atomic component or to place ions at high energies leading to escape trajectories out of the spectrometer 10, a positive electric field potential 32 is generated on the sample 14. As shown in FIG. 5, the positive electric field potential 32 on the sample 14 is pulsed

- 6 -

from about +1080 to +1350 volts prior to the arrival of the 5 kV pulsed primary ion beam 18 at the sample 14. The electric field potential 32 is maintained throughout the period of sputtering atoms from the sample 14. Thus, the positive electric field potential 32 acts to: (1) remove stray ions present before the sputtering of atoms (or ejection of the atoms by other means) from the sample 14, and also (2) to remove any secondary ions present as a consequence of the sample irradiation by the primary ion beam 18.

After removal of the unwanted ions from near the sample 14, the volume near the sample 14 contains as a residual various neutral forms of the selected atomic components which the operator desires to detect. These selected atomic components are, for example, single atoms and molecules. As shown in the view of FIG. 4, the volume containing a large portion of the selected atomic components near the sample 14 is irradiated to generate photo ions. In the illustrated embodiment (see FIGS. 4 and 5) the irradiation is performed by a laser beam pulse 34 shown in an end view cross section. As shown in FIG. 5 the laser beam pulse 34 is timed subsequent to the removal of unwanted ions from near the sample 14. As also noted in FIG. 5 the laser beam pulse 34 can comprise more than one pulse of different laser energies  $E_1$  and  $E_2$ , and this aspect of the invention will be described in more detail below. A perimeter 38 of a  $45^\circ$  conical volume is illustrated in FIG. 4, and the conical volume encompasses about one half of the ions ejected from the sample region 15 of the sample 14, assuming a cosine type distribution of the ions relative to the axis defined by the beam path 30 for the primary ion beam 18. The laser beam pulse 34 is therefore positioned with respect to this distribution to excite the maximum possible percentage of the neutral selected atomic components ejected from the sample 14.

Creation of ions of the selected atomic components is an important early step toward the objective of isolating the desired signal from unwanted noise and extraneous



- 7 -

signals measured during the final quantitative analysis. Therefore, sensitive analysis is commenced by the laser beam pulse 34 ionizing the selected atomic components to energies above the ionization potential (see FIG. 5). Significant further separation of the desired signal is achievable using two laser energies,  $E_1$  and  $E_2$  mentioned above, with the first part of the laser beam pulse 34 having an energy  $E_1$  to selectively excite the selected atomic component to an energy below the ionization level. The second laser pulse 34 has the energy  $E_2$  which ionizes the previously excited atomic component.

One form of excitation for  $E_2$  is, for example, non-resonant excitation to the ionization continuum. Because the second laser energy at  $E_2$  is not in energy resonance between an initial energy state and a final discrete state of the excited atomic component to be ionized, the cross section for the process is small; consequently, the power density required to saturate the ionization process is usually quite large. The required power can be achieved with large fixed-frequency lasers, but the drawback is that multiphoton non-resonant ionization of various unwanted species can become important. Although the multiphoton non-resonant ionization process may still have low probability relative to the single photon non-resonant ionization of the previously excited selected atomic component of interest, significant background ionization may still occur because of the much greater abundance of the majority species (e.g., atomic species of the matrix of the sample 14) in the ionization volume irradiated by the laser pulse 34.

A useful alternative for the second, ionization step at  $E_2$  involves the application of specific wavelengths chosen to connect the excited atomic level at  $E_1$ , produced by irradiation from the first laser pulse 34, with photon energy  $E_1$ , to an autoionizing level of the selected atom component. States of the autoionization type are also conventionally called "discrete states embedded in the continuum", and have the property of rapidly decaying to an ion plus a free electron. Nevertheless, cross sections for excitation to

- 8 -

these autoionization states are much larger than those for non-resonant ionization. Consequently, saturation of the second excitation step with energy  $E_2$  is possible with the use of much less power density. This reduces the probability of ionizing majority unwanted species via multiphoton non-resonant ionization processes.

Alternative modes of laser induced ionization offer other features for performing analysis of the selected atomic component in the sample 14. In cases where the extreme sensitivity of resonance ionization (discussed above) is not required, multiphoton non-resonant ionization offers some advantages. Multiphoton non-resonant ionization refers to a physical process where more than one photon is absorbed by an atomic or molecular species, with all the photons being absorbed in a single step. To achieve the desired power levels, conventional focused, high power, non-tunable lasers are typically employed. Some of the advantages of operating in a multiphoton non-resonant ionization mode are:

- (1) A rapid survey of possible impurity species of the selected atomic component in the sample 14 can be performed. Since ionization occurs without the necessity of tuning to energy resonances of each species individually of the selected atomic component, ion signals from neutral precursors of all elements present is obtained upon each occurrence of the laser pulse 34. Separation by mass is performable by a time of flight mass spectrometer alone.

- (2) A semi-quantitative comparison of relative impurity abundances can be obtained immediately. The ion-production step is a laser-based, multiphoton ionization of gas phase species released from the sample by conventional ablation processes. Variation of ionization probability from one atomic species to another can be minimized and calibrated. Dependence on the chemical environment in the sample 14 is small since the process of sputtering material depends essentially on simple momentum-transfer considerations. In contrast, in other types of ion spectroscopy (such as secondary ion

- 9 -

mass spectrometry (hereinafter, "SIMS") the ionization step itself occurs at the sample 14; and the ion production probability depends strongly on the chemical environment in the sample 14. Thus, quantitative SIMS is notoriously difficult to carry out.

(3) Molecular species can be detected. Compared with atomic species, molecular species released from the sample 14 are distributed among a relatively large number of energy levels. This distribution dilutes the population in any one state and is initially unknown. The task of studying each level with tuned resonance ionization is prohibitive. However, with non-resonant ionization, all these initial levels are ionized together. The occurrence of many intermediate near resonances in the molecular case facilitates the achievement of high ionization probability.

After generation of the ions of the selected atomic component, the ions undergo an extraction process which assists in improving the signal to noise ratio in the subsequent quantitative analysis. A predetermined electrical field 40 shown generally in FIG. 3, is generated by combining the electric field potential on the sample 14 with an electric field generated by electric field means, such as an extraction objective lens 42 having active lens elements 46, 50 and 54 (see FIG. 2). For example, the electrical field potential on the sample 14 is +1080 volts, and the potentials on the lens elements 46, 50 and 54 are +2300, -21,000 and -500 volts, respectively. The resulting predetermined electric field near the sample 14 has a potential of about +1080 volts at the sample 14 and a slowly diminishing field region 58 extending from the sample 14 over a preselected portion of the volume adjacent to the sample 14. The slowly diminishing electrical field derives primarily from the field penetration of the highly negative potential of the lens element 50. The field potential over the width of the cross section of the laser beam pulse 34 shown in FIG. 3, is about 78 volts but can be readily modified by manipulating the various potentials on the sample 14 and the lens elements 46, 50 and 54.

- 10 -

The final ions generated from the neutral atomic components within the slowly diminishing field region 58 have a relatively narrow spread of electric potential across the volume, enabling more complete transmission and improved accuracy of energy analysis of the ions in the step of quantitative EARTOF analysis. At the same time, the high negative potential on the lens element 50 also enables the efficient collection of the ions and leads to improved signal to noise ratio. The use of a high negative potential on the lens element 50 has further advantages associated with ion beam focusing. This latter feature will be discussed in more detail hereinafter.

Contiguous to the slowly diminishing field region 58 and extending along particular directions substantially outside the volume and away from the sample 14 is a rapidly diminishing field region 62 shown in FIG. 3. This strongly negative field region acts on the ions entering this region 62 and begins the ion extraction process. As mentioned above, the strong negative field helps increase the photo ion collection efficiency and improves consequent signal to noise ratio. Extraction of the photo ions is accomplished by an extraction lens system, which comprises the extraction objective lens 42 discussed hereinabove and a collimator lens system 84, having elements 85, 86 and 87.

During operation of the spectrometer 10, contaminants are deposited on surfaces near the sample 14, and can result in the generation of unwanted secondary ions and consequent detection of unwanted signals. These unwanted signals typically arise from deposition of material on portions of the extraction objective lens 42 and redeposition on the sample 14 as a contaminant, which is uncharacteristic of the true sample chemistry. These unwanted signals can be reduced by minimizing deposition of material on the nearby lens elements 46, 50 and 54 of the extraction objective lens 42. This minimization of material deposition is accomplished by forming one or more of the lens elements 46, 50 and 54 into appropriately shaped structures. For example, as best

- 11 -

shown in FIGS. 1 and 2 the lens elements 46, 50 and 54, each comprises truncated conical structures, minimizing the surface area exposed to the flux of particles emanating from the area including the sample 14. In particular, the lens element 46 nearest the sample 14 has a leading knife edge 108 for the conical structure, which further reduces the surface area exposed to the particle flux from the area, including the sample 14. The thicker structure used for the lens element 50 is designed to reduce the secondary electron emission which can arise from operation at a high negative electric field potential. However, since the redeposition problem rapidly diminishes with distance from the sample 14, any redeposition problem associated with the lens element 50 is much less than associated with the closer lens element 46.

The redeposition problem is further minimized by control of the electric field potential applied to the extraction objective lens 42. In the illustrated embodiment the electric field potential applied to the lens element 46 nearest the sample 14 is higher than the electric field potential on the sample 14, as opposed to the previously mentioned secondary ion mass spectrometer (SIMS), wherein the electric field potential is strongly negative with respect to the sample 14. The result is the flux of contaminant ions able to reach the lens element 46 is substantially limited in the present invention.

The extraction objective lens 42 and the collimator lens system 84 cooperate to extract neutral atomic components, which have been ionized by the laser beam pulse 34. The elements 85, 86 and 87 of the collimator lens system 84 comprises a set of conventional aperture einzel lenses. The extraction objective lens 42 and the collimator lens system 84 act to transform the trajectory pattern of the selected atomic component ejected from the sample 14 into a highly collimated ion beam 88 (hereinafter, the "ion beam 88") traveling along a third path 90. Thus, the extraction objective lenses 42 and 84 not only function to focus the primary ion beam 18 onto the sample 14, but also

- 12 -

operate to extract the photo ions and provide the necessary collimation for subsequent quantitative EARTOF analysis. Lens element systems 94 and 98 provide additional focusing of the ion beam 88 prior to input to energy analyzer means, such as electrostatic analyzers 102 and 104 shown in FIGS. 1 and 6.

The EARTOF quantitative analysis of the illustrated embodiment is performed in a spectrometer detector region 105 using the electrostatic analyzers 102 and 104 and an associated telescopic lens 110. The construction of this portion of the spectrometer 10 allows the reduction of the spread in time-of-flight for the ions undergoing analysis and includes structural features which attenuate various sources of noise, with both features leading to improved detection sensitivity. Another important feature is the use of  $180^\circ$  sections for the electrostatic analyzers 102 and 104 which provides a significant refocusing feature. Thus, for those ions having an angular deviation from perpendicularity with respect to the entry window plane of the electrostatic analyzer 102, the impact point at the exit window plane occurs very close to that of an ideal orbit. As a consequence, quite small entry window sizes can be utilized, and an improved attendant energy resolution results. The electrostatic analyzers 102 and 104 are constructed as  $180^\circ$  spherical electrostatic deflectors generating electric field potentials for energy analyzing the ion beam 88. These features give rise to the energy and angular refocusing properties of the illustrated EARTOF mass spectrometer.

The electrostatic analyzers 102 and 104 include resistive disk means, such as a flat resistive disk boundary plate 112 (hereinafter, "resistive plate 112") shown in a plan view in FIG. 7. The resistive plate 112 is disposed between an inner conducting hemisphere 116 and an outer conductor 120. Details of functionality of the resistive plate 112 and its method of manufacture will be discussed hereinafter. In the preferred embodiment, the outer conductor 120 is a conducting hemisphere shape, but in another

- 13 -

form of this invention the outer conductor 120 can be a metallic band about the circular perimeter of the resistive plate 112. The outer conductor 120 is preferably constructed of a highly transparent metal mesh formed into the hemispherical shape. The open nature of the metal mesh minimizes the probability that ions uncharacteristic of the selected atomic component and which have escape trajectories leading out of the electrostatic analyzers 102 and 104 will be detected by a detector 106.

The ion beam 88 is input to the electrostatic analyzer 102 through a first entry window 124 which can be relatively narrow as discussed hereinbefore. A point focus of the ion beam 88 can be used advantageously to provide good energy resolution, thus minimizing energy variations resulting from the ions entering the electrostatic field off center. In addition this feature minimizes electric field fringe distortions whose magnitude is approximately proportional to the size of the opening of the entry window 124. In a similar manner a second exit window 136 of the electrostatic analyzer 104 has a relatively narrow opening, which gives rise to the same types of advantages attendant the narrow opening of the first entry window 124. The electrostatic analyzers 102 and 104 both have relatively large radial gaps between the inner conducting hemisphere 116 and the outer conductor 120. This relatively large radial gap accommodates a large range of charged particle energies within the energy analysis bandpass of the electrostatic analyzers 102 and 104, thereby improving the total collected signal and the signal to noise ratio.

A first exit window 128 and a second entry window 132 (see FIGS. 1 and 6A) both have relatively wide openings to accommodate the angularly divergent ions having different energies associated therewith. The electric field equipotentials near the various windows are, however, substantially ideal as a consequence of using the resistive plate 112 (see FIGS. 6A and 7), which provides predetermined electric field boundary

- 14 -

conditions to achieve the required electric field potential. Structural details and a method of preparation of the resistive plate 112 will be discussed hereinafter.

The orbits of the ions vary with kinetic energy, and for a particular electric field potential and kinetic energy,  $E_0$ , a circular orbit 133 is defined (see FIG. 6A). Therefore, for those ions having larger kinetic energy  $E'$ , such that  $E'/E_0 > 1$ , an orbit 134 is elliptical and has a larger arc terminating on the outer edge of the first exit window 128. Likewise for  $E'/E_0 < 1$ , a smaller arc terminates on the inner edge of the first exit window 128. If the orbits of the ions were allowed to complete a  $360^\circ$  arc, the known properties of trajectories in a  $1/r$  electric field potential would indicate the return of the ion to the same starting point for ion energies below the energy escape values.

Furthermore, the time to complete one orbit for ions having substantially the same energy, but entering the electrostatic analyzer 102 with an angular deviation from the perpendicular to the plane of the first entry window 124, is weakly dependent on the angle of deviation for small angles of deviation. For the  $180^\circ$  spherical electrostatic analyzer 102, there is a focus at the plane of the exit window 128 and beyond that plane, the particle orbits diverge in the manner illustrated in FIG 6B. Also, note the ions having orbits deviating from the perpendicular to the plane do not pass through the plane of the exit window 128 at the center of the exit window 128, but rather pass inside the center. However, as seen in FIG. 6A, this result is avoided in the electrostatic analyzers 102 and 104 by including the telescopic refocusing lens system 110 (hereinafter "lens system 110"). The components of the lens system 110 include two electrostatic lens sets 140, which are identical to one another in the preferred embodiment. More particularly each of the lens sets 140 are aperture einzel-lenses utilizing central elements at negative electric field potential.



- 15 -

The resistive plate 112, together with the inner conducting hemisphere 116 and the outer 120 conductor, performs the function of a spherical electrostatic prism which provides predetermined electric field boundary conditions to achieve the stringent electric field potential required for the electrostatic analyzers 102 and 104. In order to maintain precise control of the high energy (kV level) ions and thereby isolate the desired signal from unwanted signals and noise, kV level voltages are usually applied across the resistive plate 112 to achieve the desired deflecting forces. The resistive plate 112 is also operated in a vacuum, and to maintain this vacuum the material should exhibit low vapor pressure, even when heat is generated during use. The resistive plate 112 also should be able to readily dissipate heat generated in order to avoid significant dimensional changes and possible material failure. These operating features make difficult the manufacture of the resistive plate 112 from bulk materials of the appropriate high resistivity. In the embodiment illustrated in FIG. 7, the resistive plate 112 comprises an insulator substrate 144, such as machinable glass ceramic of very high resistivity. Disposed on the insulator substrate 144 is a preselected thick film configuration 148 having selected electrical resistivity characteristics enabling generation of the previously mentioned predetermined electric field boundary conditions, responsive to an electrical current applied to the preselected thick film configuration 148. The resistive plate 112 therefore serves to provide substantially ideal electric field boundary conditions between the inner conducting sphere 116 and the outer conductor 120 of the electrostatic analyzers 102 and 104.

The manufacture of the resistive plate 112 involves deposition of resistive thick films using screen printing methods. In the preferred embodiment the resistive thick film is derived from an oxide paste, such as a bismuth-ruthenium oxide based material manufactured under the trade name of "BIROX" by Du Pont Corp. The oxide paste is

- 16 -

applied to the insulator substrate 144 through a prepared mask screen (not shown). The screen printing method enables deposition of thick films with complex spatial patterns to accommodate the desired predetermined electric field boundary conditions. Metallic pastes are also applied to the insulator substrate 144 to establish an electrode contact for applying electric current to the resistive portion of the preselected thick film configuration 148.

To achieve the predetermined electric field boundary conditions, given the shapes of the entry windows 124 and 132 and the exit windows 128 and 136 for the electrostatic analyzers 102 and 104, respectively, the fabrication steps are: (1) prepare the correct shape and size of the insulator substrate 144 suitable for depositing the thick films thereon, (2) apply a thin conducting Ag/Pd based paste 156 to the insulator substrate 144, (3) firing the insulator substrate 144 at a temperature appropriate to achieve the desired electrical and mechanical properties, typically about 800°C with the conductive thick film configuration applied from step two above, (4) applying through the mask screen a resistive oxide paste (such as BIROX) to form an annular and spherical triangle configuration 152 shown in FIG. 7; also a thin layer 154 of the resistive oxide paste is applied to the upper and lower surfaces of the entry windows 124 and 132 and the exit windows 128 and 136, and (5) firing the assembly to form the final, fixed high electrical resistivity for the preselected thick film configuration 148. The design of the preselected thick film configuration 148 is based on the geometry of the electrostatic analyzer 102 or 104, including the shape and size of the various windows. Calculation of the desired form of the preselected thick film configuration 148 is achievable using specialized mathematical analysis developed for this purpose.

In another form of the invention the general ability to provide predetermined electric field boundary conditions using the preselected thick film configuration 148 has

- 17 -

general applications. These applications arise when there is a need for electric field means generating an undistorted electric field potential, particularly near structural anomalies, such as holes and protrusions. Important applications also arise for instances when electric field regions are defined by irregular shapes and in cases where the designer wishes to modify selected portions of the electric field.

An additional feature of the spectrometer 10 is the application of a coating applied to reduce or minimize effects of using radiation beams in the spectrometer 10. For example, there can be a buildup of excess charge on portions of the spectrometer 10, causing electrostatic anomalies which deflect various charged particles away from desired trajectories and even causing damage preferentially to selected locations.

In another form of the invention coatings can be applied which are particularly resistant to laser ionization and are typically used on conductive elements near the sample 14. This type of coating is applied to selected portions of various ones of the lens system elements of the spectrometer 10. Examples of ionization resistant coatings comprise metals which include: Au, Ag, Cu, Pd, Pt, Ru, Sn, Y and Zr. Other materials also can be utilized to reduce detrimental effects and are compatible with the performance specifications of the spectrometer lens system, while performing in accordance with the desired coating requirements. The preferred gold coating is applied to the selected lens element to provide protection from interactions with various radiation beams, such as the laser beam pulse 34, the primary radiation beam 18 and any secondary ions, including the selected atomic components.

#### Other Example Modes of Operation of the Spectrometer

Because of its unique design, the spectrometer 10 can be operated in a variety of modes, thus making it a versatile instrument for determining surface properties of the sample 14. For example, in the SIMS operating mode, mass spectrometric studies

- 18 -

of sputtered secondary ions are carried out. Removal of material from the surface of the sample 14 by beams of atoms, ions, electrons or by photon beam bombardment or by fission fragments (plasma desorption mass spectrometry), results in the ejection of a certain fraction of the sample 14 in the form of secondary ions. The spectrometer 10 can be operated in the SIMS mode, leaving the sample 14 at a fixed potential and dispensing with the laser pulses 34. Positive and negative secondary ions can be mass analyzed and detected using the electrostatic analyzers 102 and 104 and the associated resistive plate 112.

In another form of the invention the spectrometer 10 is operated in the Ion Scattering Spectroscopy ("ISS") mode. The ISS mode is an important method for obtaining surface composition and adsorbate structural information on the sample 14. The design of the spectrometer 10 allows it to be operated as an ISS instrument by taking advantage of the fact that the incoming primary ion beam 18 is directed normal to the sample 14, while the path of ion travel during time of flight measurements is along the third path 90, also normal to the sample 14. In the ISS mode the resistive plate 112 is switched off while an ion detector 160 shown in FIG. 1 is activated to detect the ion beam 88 allowed to pass thereto (See FIG. 1). Back scattered ions from the primary ion beam 18 are energy analyzed in the time of flight portion of the spectrometer by measuring their arrival time at the ion detector 160 in a conventional manner.

In addition to functioning as positive and negative ion energy analyzers, the electrostatic analyzers 102 and 104, along with the resistive plate 112, are adapted to function as electron energy analyzers. They therefore can be used for generally performing charged particle energy analysis, including energy analysis of Auger, X-ray photoelectron, ultraviolet photoelectron and synchrotron radiation photoelectron spectroscopy. Provisions for appropriate sample illumination devices such as electron

- 19 -

guns, X-rays or U.V. photon sources can be made in a conventional manner. The following example is merely illustrative.

### E X A M P L E

The preferred embodiment has been used to perform depth profiling analyses on high purity silicon wafers which had been implanted with  $^{56}\text{Fe}$  at an energy of 60kV. This chemical system was chosen to illustrate advantages of analysis for the spectrometer 10 over conventional SIMS which experiences problems associated with the substantial mass equivalent of the Fe and  $\text{Si}_2$  dimer species. Both of these atomic components appear at the nominal mass fifty-six position.

In the measurements cited here, the Fe concentration at the peak of the concentration profile vs. depth was reliably estimated at 400 ppb through the use of standard ion implantation range data. Based on that calibration, the following data were measured in the spectrometer 10.

### Princial Results

Sensitivity limit:	<2 ppb for $^{56}\text{Fe}$ impurity in silicon 0.5 ppb for $^{54}\text{Fe}$ impurity in silicon
Collection efficiency:	About 8% (atoms detected per atom removed from sample)

### Measurement Parameters

Ion beam area:	0.05 mm <sup>2</sup>
Ion beam current:	2 A
Ion beam energy:	5 kV
Measurement time:	1000 seconds
Monolayers removed:	0.86
Signal/noise:	1
Raster area:	4mm <sup>2</sup>

While preferred embodiments of the present invention have been illustrated and described, it will be understood that changes and modifications can be made therein without departing from the invention in its broader aspects. Various features of the invention are defined in the following claims.

- 20 -

What Is Claimed Is:

1. A method of efficiently extracting for quantitative spectroscopic analysis a selected atomic component removed from a sample, comprising the steps of:

generating near said sample a volume containing said selected atomic component;

applying a predetermined electric field near said sample, said predetermined electric field comprising a slowly diminishing field region extending from said sample over a preselected portion of said volume adjacent said sample and a rapidly diminishing field region extending along particular directions outside said preselected volume portion and extending contiguous to said slowly diminishing field region;

ionizing said selected atomic component substantially in said slowly diminishing field region; and

extracting said ionized atomic component responsive to entering said rapidly diminishing field region, said extracted atomic component subsequently undergoing said quantitative spectroscopic analysis.

2. The method as defined in Claim 1 wherein said slowly and rapidly diminishing field regions comprise electric field potentials decreasing with the perpendicular distance from said sample.

3. The method as defined in Claim 2 wherein said electric field potential diminishes about 5 to 100 volts over said slowly diminishing field region.

4. A method of efficiently extracting for quantitative spectroscopic analysis a selected atomic component removed from a sample, comprising the steps of:

generating near said sample a volume containing said selected atomic component;

generating an electric field on said sample for selectively repelling ions from the vicinity of said sample;

- 21 -

applying a predetermined electric field near said sample, said predetermined electric field comprising a slowly diminishing field region extending from said sample over a preselected portion of said volume adjacent said sample and a rapidly diminishing field region extending along particular directions outside said preselected volume portion and extending contiguous to said slowly diminishing field region;

ionizing said selected atomic component substantially in said slowly diminishing field region; and

extracting said ionized atomic component responsive to entering said rapidly diminishing field region, said extracted atomic component subsequently undergoing said quantitative spectroscopic analysis.

5. The method as defined in Claim 4 wherein said step of generating said electric field comprises applying a pulsed electric field to said sample while applying said predetermined electric field, said pulsed electric field repelling ions from the vicinity of said sample.

6. A method of efficiently extracting for quantitative spectroscopic analysis a selected atomic component removed from a sample, comprising the steps of:

generating near said sample a volume containing said selected atomic component;

applying a predetermined electric field near said sample, said predetermined electric field comprising a slowly diminishing field region extending from said sample over a preselected portion of said volume adjacent said sample and a rapidly diminishing field region extending along particular directions outside said preselected volume portion and extending contiguous to said slowly diminishing field region, said step of applying a field performable by electric field means having structures appropriately shaped for minimizing redeposition probability of the atoms from said electric field means onto said sample;

- 22 -

ionizing said selected atomic component substantially in said slowly diminishing field region; and

extracting said ionized atomic component responsive to entering said rapidly diminishing field region, said extracted atomic component subsequently undergoing said quantitative spectroscopic analysis.

7. The method as defined in Claim 6 wherein said appropriately shaped structures comprise truncated conical portions.

8. A method of efficiently extracting for quantitative spectroscopic analysis selected ions derived from laser excitation of a selected atomic component removed from portions of a sample, comprising the steps of:

generating a volume containing said selected atomic component near said sample;

applying a predetermined electric field near said sample, said predetermined electric field comprising a slowly diminishing field region extending from said sample over a preselected portion of said volume adjacent said sample and a rapidly diminishing field region extending along particular directions outside said preselected volume portion and extending contiguous to said slowly diminishing field region;

ionizing said selected atomic component to said selected ions substantially in said slowly diminishing field region; and

extracting said selected ions responsive to entering said rapidly diminishing field region, said extracted ions undergoing said quantitative spectroscopic analysis.

9. The method as defined in Claim 8 wherein said step of generating a volume of said selected atomic component comprises generating an energetic particle beam and bombarding said sample with said particle beam.



- 23 -

10. The method as defined in Claim 9 wherein said energetic particle beam comprises at least one of an ionized particle beam, a neutral particle beam and a photon beam.

11. The method as defined in Claim 8 wherein said step of ionizing comprises applying at least one laser beam pulse to said atomic component, said laser beam pulse having a predetermined energy spectrum for achieving selected non resonance ionization, resonance and autoionization resonance states for said selected atomic components.

12. A method for quantitative spectroscopic analysis of a sample using a spectrometer to measure the quantity of a selected atomic component removed from said sample by radiation beam bombardment, comprising the steps of:

bombarding said sample with said radiation beam thereby generating a volume near said sample containing said selected atomic component;

applying at least one laser beam pulse to said atomic component volume, said laser beam pulse having a predetermined energy spectrum for achieving selected autoionization resonance states for said selected atomic component;

extracting said autoionized selected atomic component from said volume near said sample; and

detecting said autoionized selected atomic component using said spectrometer for measuring the relative quantity of said selected atomic component in said sample.

13. A lens system in a spectrometer for efficiently manipulating a primary radiation beam and ionized forms of a selected atomic component derived from a sample for analysis in a detector region of said spectrometer, comprising:

means for deflecting said primary radiation beam from a first path onto a second path incident substantially perpendicular to said sample;

- 24 -

means for focusing said primary radiation beam onto said sample to produce said selected atomic component; and

means for extracting ionized forms of said selected atomic component along a third path substantially perpendicular to said sample, said third path comprising at least said second path and leading to said spectrometer detector region.

14. The lens system as defined in Claim 13 wherein said primary radiation beam comprises an ion beam and said deflecting means comprises an electric field generating device adapted for applying a pulsed electric field to said ion beam.

15. The lens system as defined in Claim 13 wherein said selected atomic components are ionizable by a laser beam pulse and the elements of said lens system have an ionization resistant covering for protecting said lens system from interactions with at least one of said primary radiation beam, said selected atomic components and said laser beam pulse.

16. The lens system as defined in Claim 13, said ionization resistant covering selected from the group consisting of Au, Ag, Cu, Pd, Pt, Ru, Sn, Y and Zr.

17. The lens system as defined in Claim 13 further including a coating selectively applied to portions of said lens system to eliminate electrostatic charge buildup.

18. The lens system as defined in Claim 13 wherein said means for focusing and said means for extracting comprise a combination single negative DC electrostatic lens.

19. An apparatus adapted for performing energy analysis on ions for quantitative analysis measurements by a mass spectrometer, comprising:

- 25 -

an inner conducting hemisphere and an outer conductor adapted to provide a required electric field potential therebetween for performing said energy analysis of said ions; and

resistive disk means disposed between said inner conducting hemisphere and said outer conductor for providing predetermined electric field boundary conditions to achieve said required electric field potential, said resistive disk means including particle entrance and exit windows and further comprising an insulator substrate and disposed thereon a preselected thick film configuration having selected electrical resistivity characteristics enabling generation of said predetermined electric field boundary conditions responsive to an electrical current applied to said thick film configuration.

20. The apparatus as defined in Claim 19 wherein said outer conductor comprises an outer conducting hemisphere.

21. A method of preparing a device useful for providing predetermined electric field boundary conditions for shaping a required electric field potential, comprising the steps of:

preparing an insulator substrate suitable for depositing a thick film thereon;

depositing a preselected configuration of said thick film on said insulator substrate to achieve said predetermined electric field boundary conditions, said depositing step further comprised of placing a prepared mask screen over said insulator substrate and applying a resistive paste and a conductive paste through the openings in said prepared mask screen onto said insulator substrate; and

selectively firing the combination of said pastes and said insulator substrate, forming an electrically active thick film configuration having a low vapor pressure.

22. The method as defined in Claim 21 wherein said depositing step comprises the following steps taken in various selected orders: placing said prepared mask screen

- 26 -

over said insulator substrate, applying a conductive paste through said mask screen and applying a resistive paste through said prepared mesh screen.

23. A device for providing predetermined electric field boundary conditions for achieving a required electric field potential generated by electric field means, comprising:

an insulator substrate;

means for applying an electrical current; and

a preselected thick film configuration disposed on said insulator substrate and adapted for coupling to said electric field means, said thick film configuration having selected electrical resistivity characteristics enabling provision of said predetermined electric field boundary conditions responsive to said electrical current applied to said thick film configuration.

24. A method for performing quantitative spectroscopic analysis by energy and angular refocusing of ions of a selected atomic component from a sample and sensing the ions with a detector, comprising the steps of:

generating near said sample a volume containing said selected atomic component;

ionizing said selected atomic component in said volume near said sample;

generating electrical field conditions for extracting said ionized atomic component;

inputting said extracted ionic atomic component to an electrostatic analyzer;

applying a first 180° spherical electrostatic field to said input ionic extracted atomic component for energy analyzing said ionic component and generating an output beam;

refocusing said output beam using a telescopic electrostatic lens system to provide a refocused beam; and,

- 27 -

applying a second 180° spherical electrostatic field to said refocused beam for completing said energy analyzing process and focusing said energy analyzed beam on said detector.

25. An ion spectrometer having a lens system for efficiently manipulating a primary radiation beam, backscattered primary ions and secondary ions of atomic components ejected from a sample, comprising:

means for deflecting said primary radiation beam from a first path onto a second path incident substantially perpendicular to said sample;

means for focusing said primary radiation beam onto said sample to produce said secondary ions;

means for selectively extracting said backscattered and said secondary ions along a third path substantially perpendicular to said sample, said third path comprising at least second path; and

means for selectively detecting said extracted backscattered and secondary ions along said third path, said detecting means selectively measuring time of flight and flux of said extracted backscattered and secondary ions and said primary radiation beam.

26. A spectrometer for performing energy analysis on charged particles for quantitative spectroscopy, comprising:

an inner conducting hemisphere and an outer conductor adapted to provide a required electric field potential therebetween for performing said energy analysis of said charged particles; and

resistive disk means disposed between said inner conducting hemisphere and said outer conductor for providing predetermined electric field boundary conditions to achieve said required electric field potential, said resistive disk means including particle entrance and exit windows and further comprising an insulator substrate and disposed thereon a

- 28 -

preselected thick film configuration having selected electrical resistivity characteristics enabling generation of said predetermined electric field boundary conditions responsive to an electrical current applied to said thick film configuration.

27. The spectrometer as defined in Claim 26 wherein said charged particles selectively comprise positive ions, negative ions and electrons.

28. A method for performing quantitative spectroscopy by energy analyzing charged particles emanating from a sample and sensing said charged particles with a detector, comprising the steps of:

generating said charged particles emanating from said sample;

applying electric field conditions to said charged particles for extracting said charged particles;

inputting said extracted charged particles to an electrostatic analyzer;

applying a first 180° spherical electrostatic field to said input charged particles for energy analyzing said charged particles and generating an output beam;

refocusing said output beam using a telescopic electrostatic lens system to provide a refocused beam of said energy analyzed charged particles; and

applying a second 180° spherical electrostatic field to said refocused beam for completing said energy analyzing and focusing said energy analyzed beam on said detector.

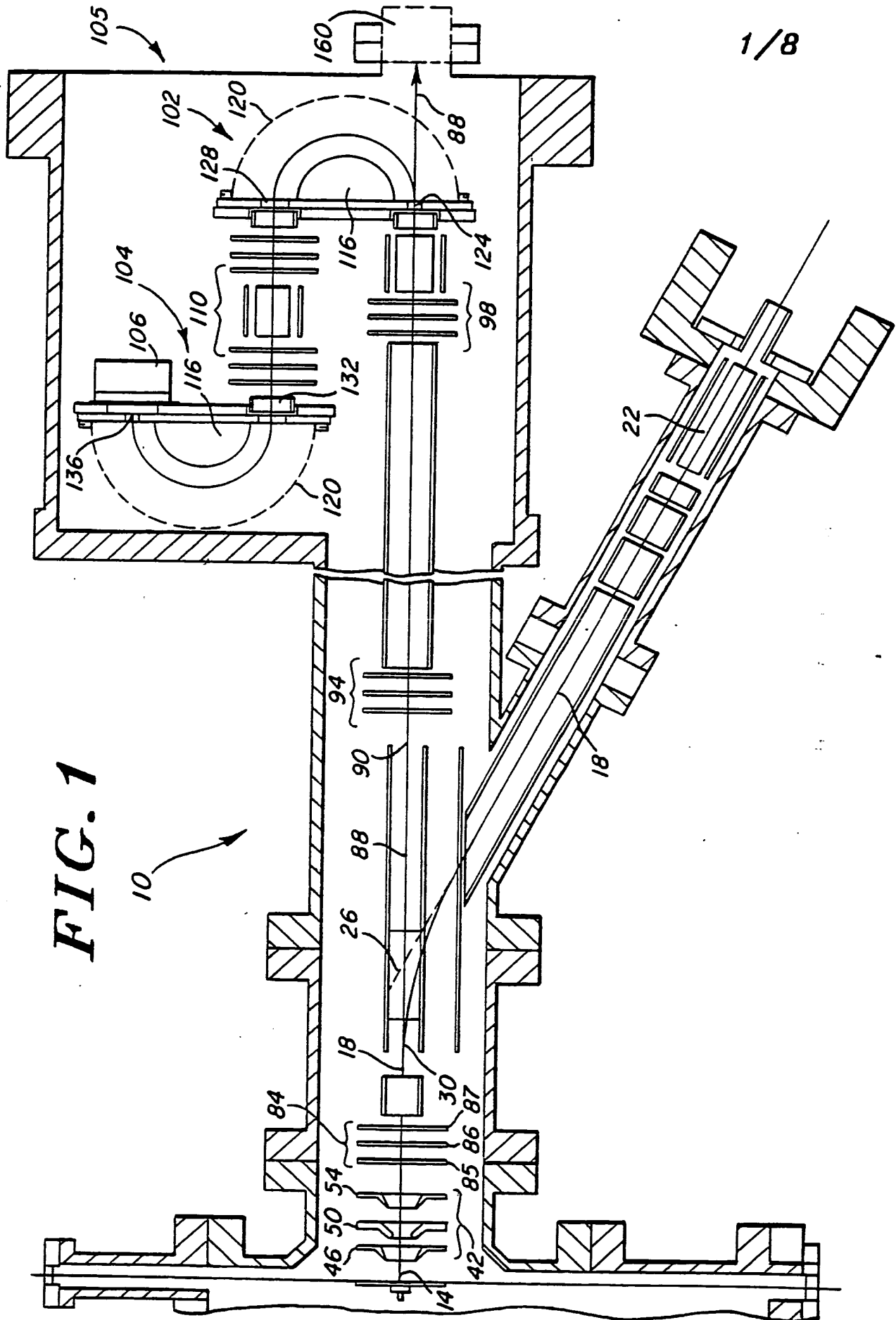


FIG. 1

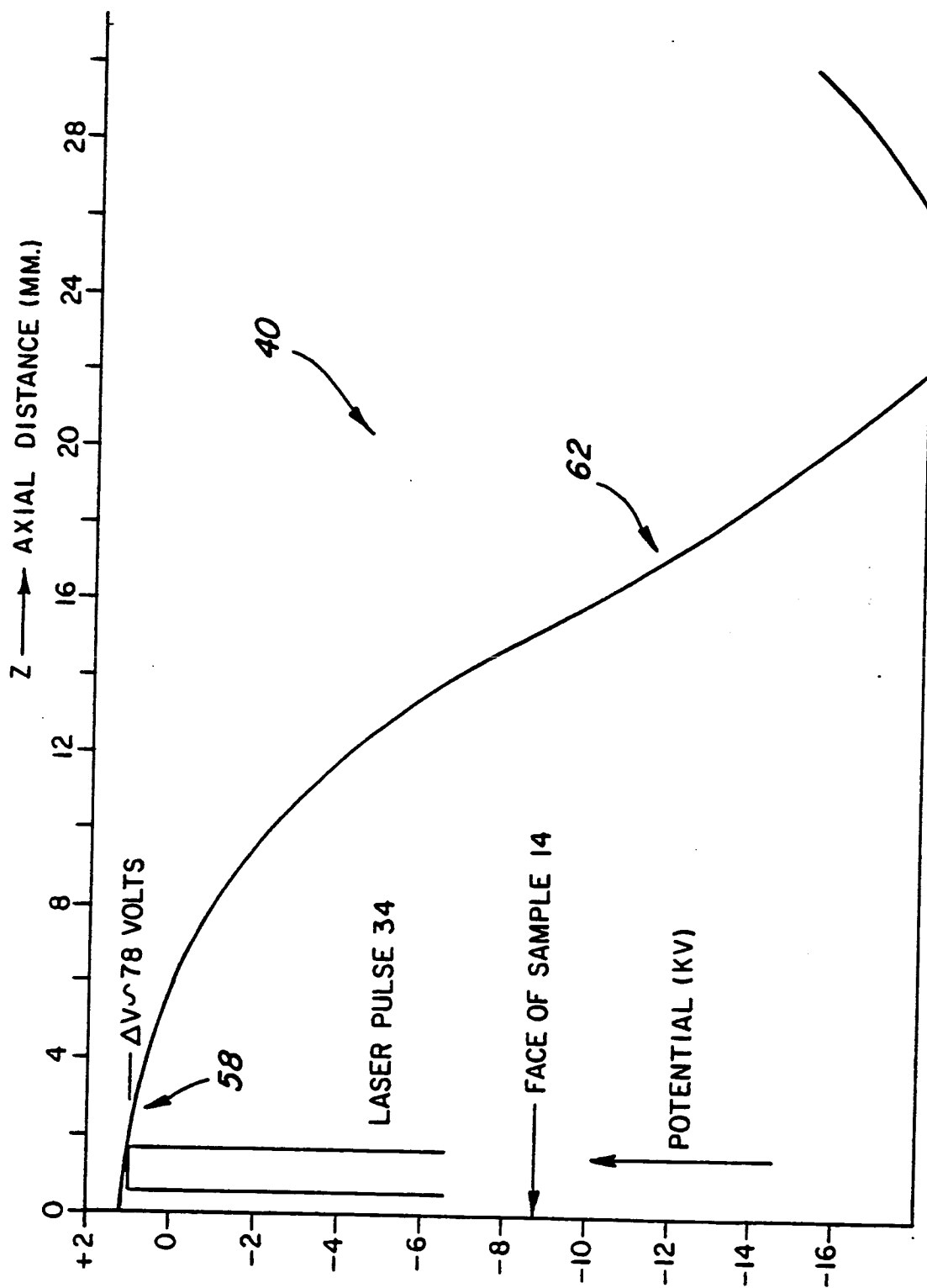
1/8



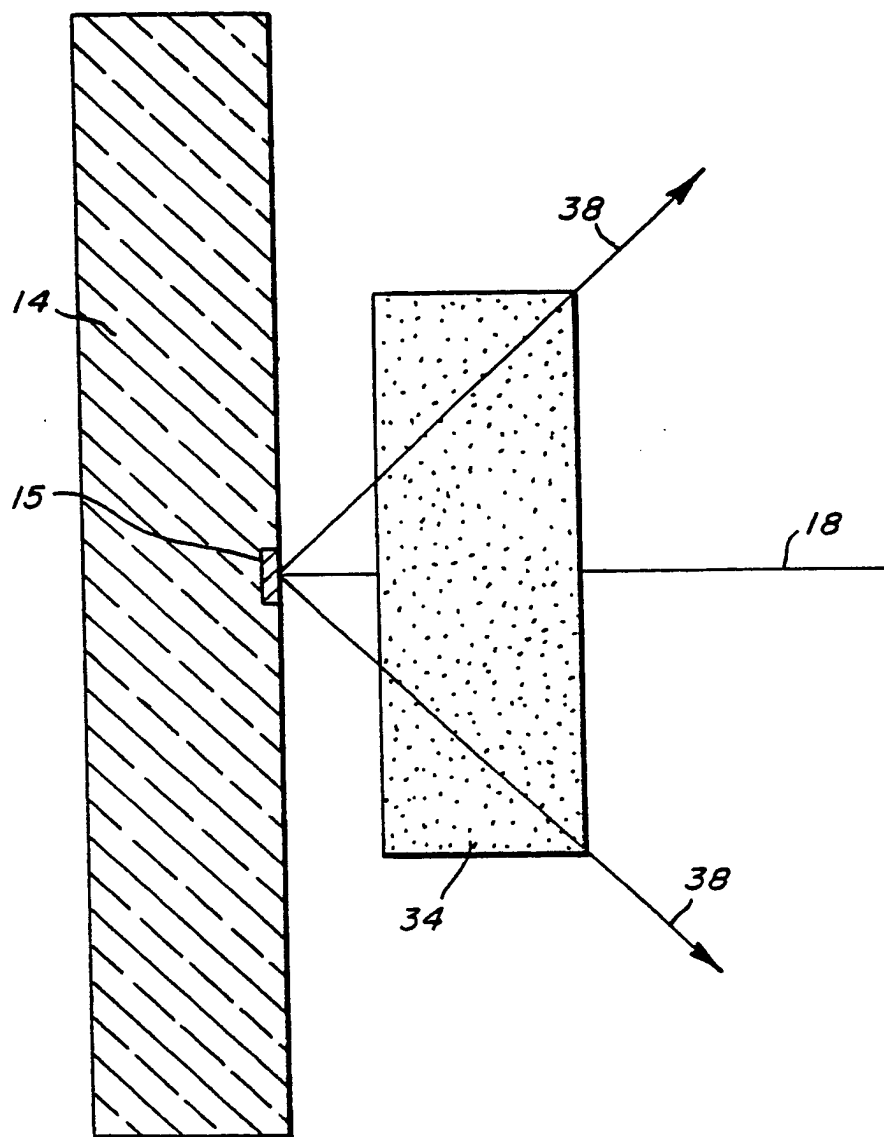


3/8

FIG. 3



4/8

*FIG. 4*

SUBSTITUTE SHEET

5/8

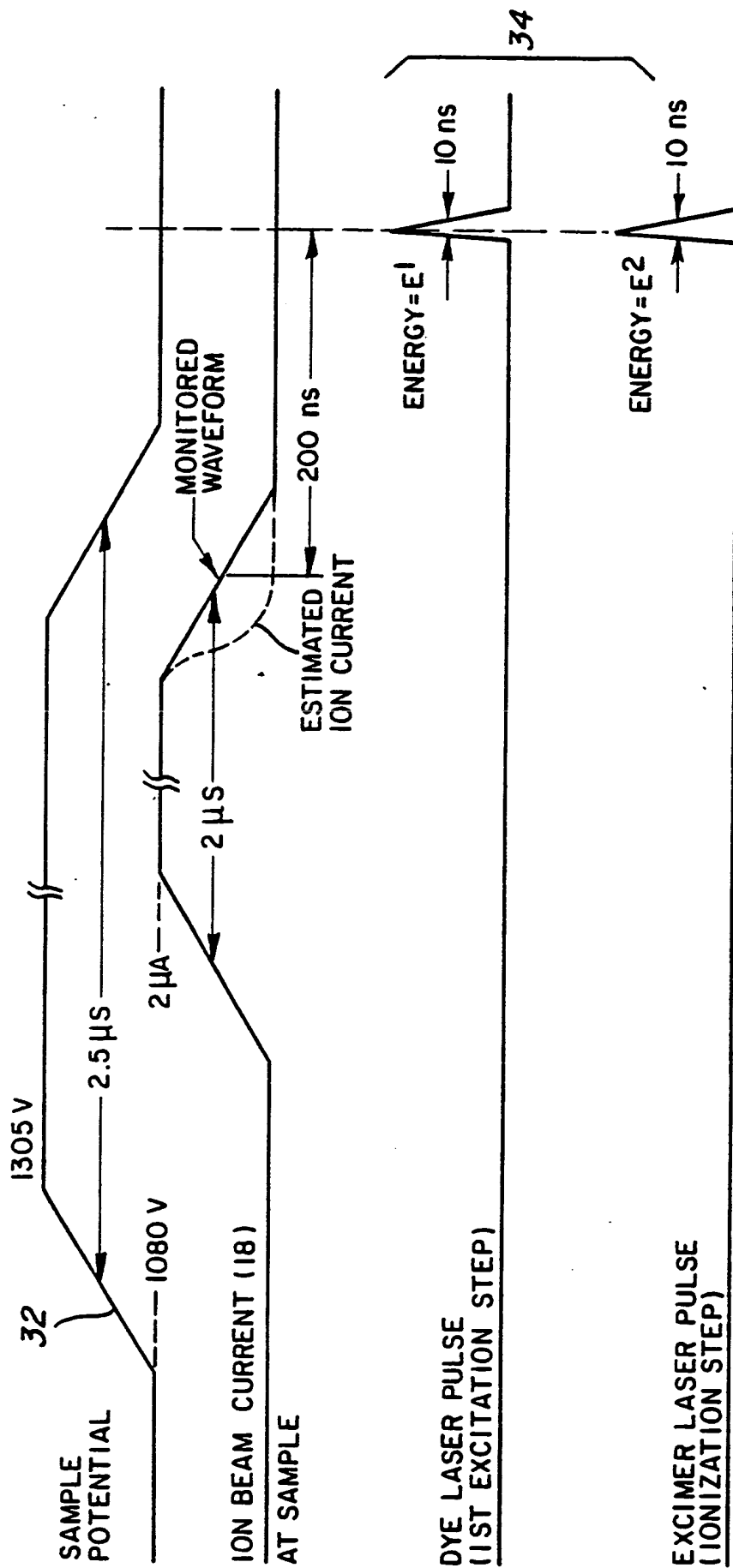
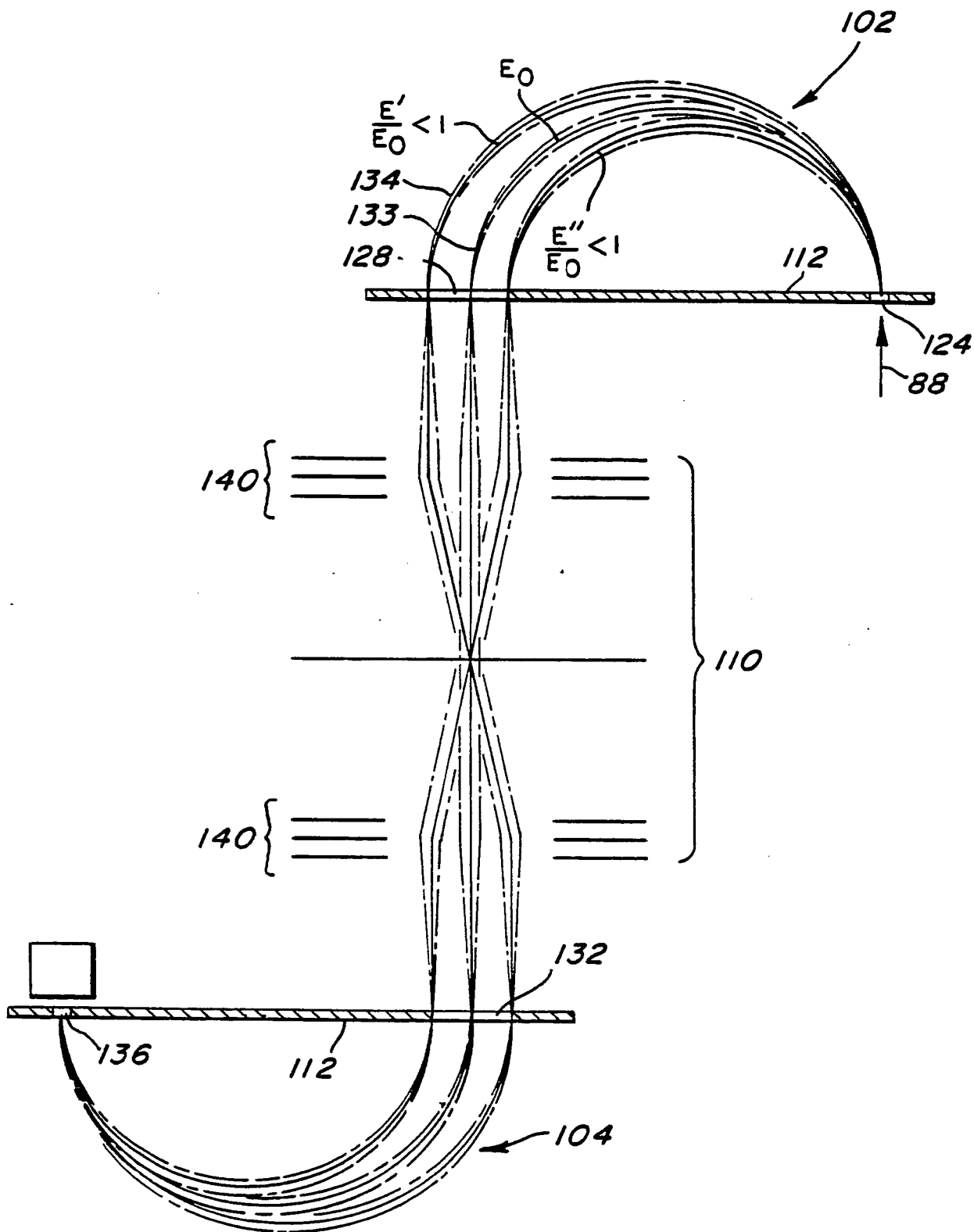


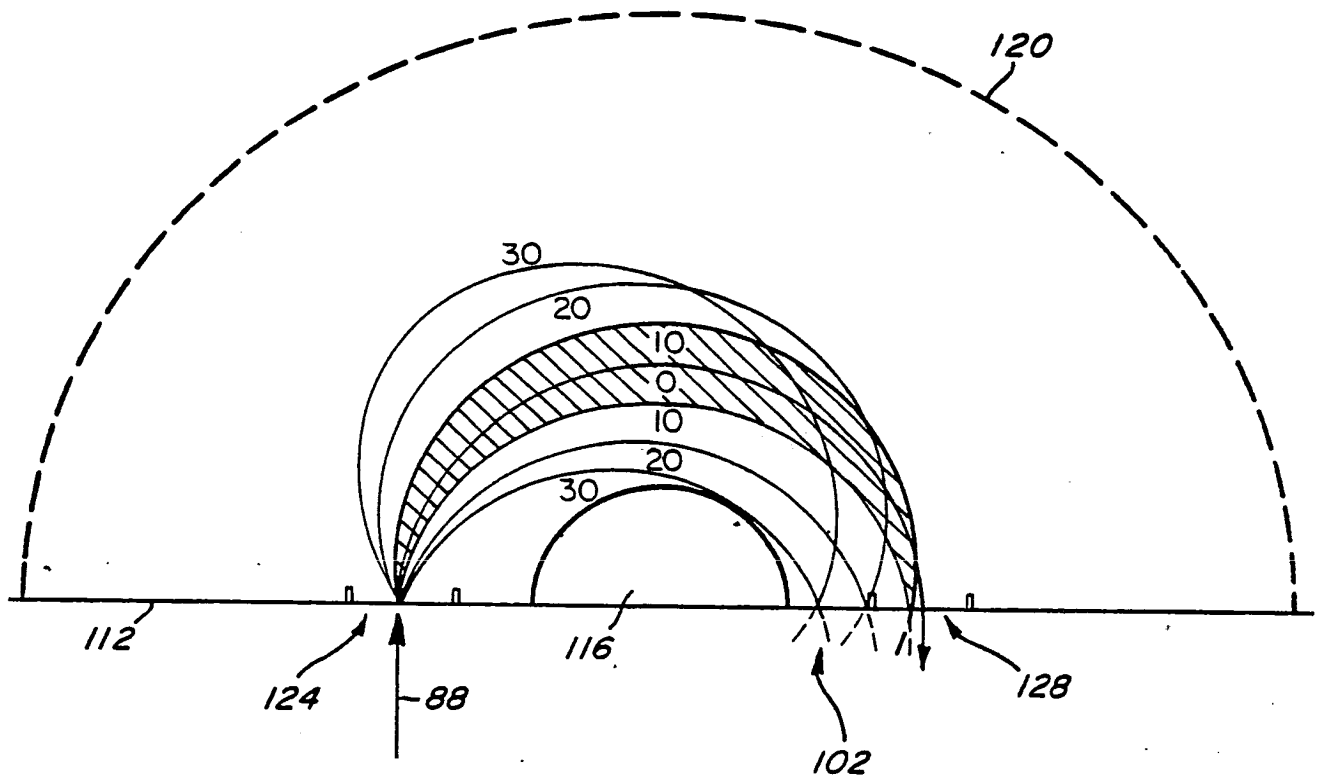
FIG. 5

6/8

**FIG. 6A**

SUBSTITUTE SHEET

7/8

**FIG. 6B**

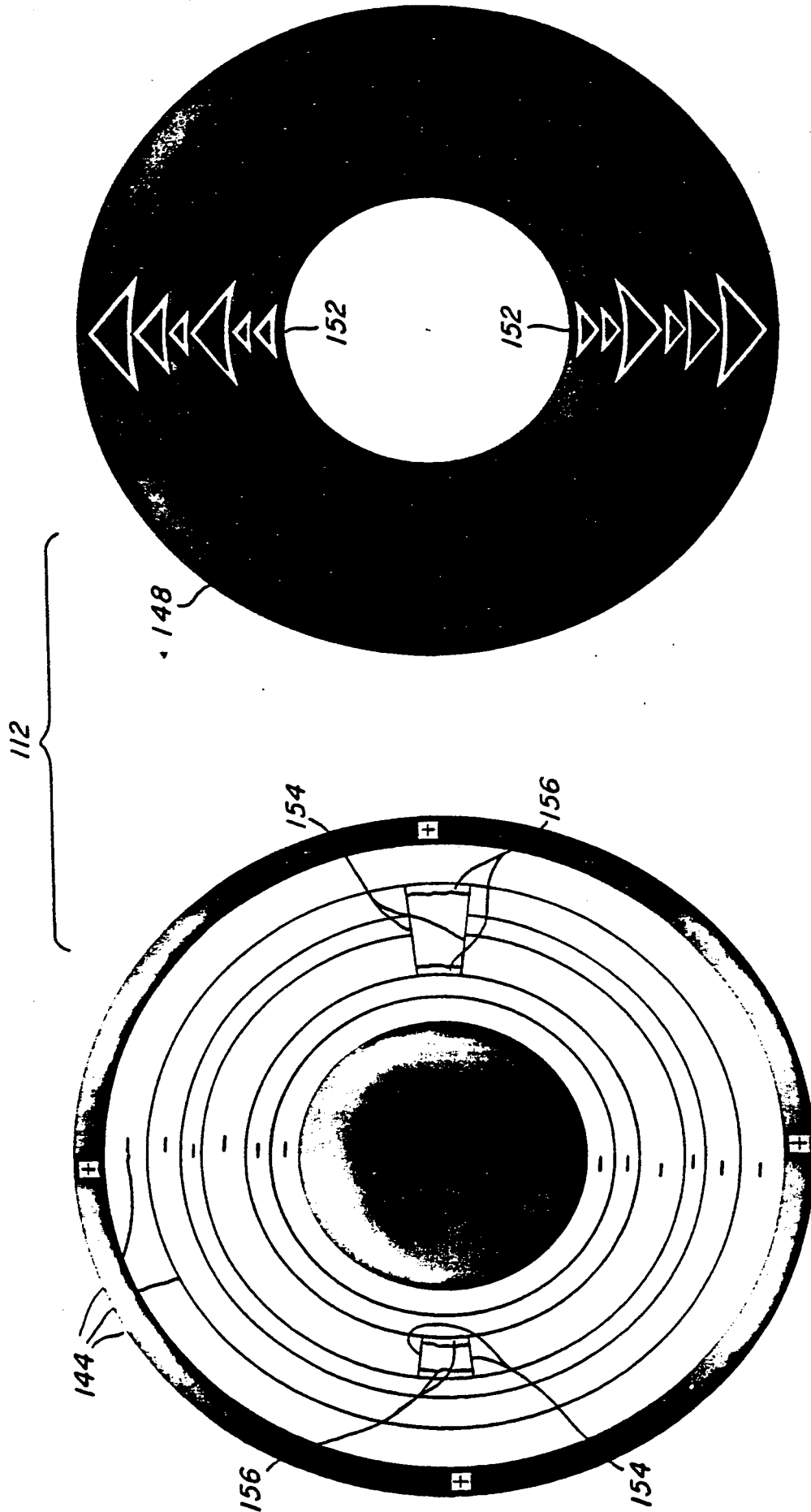
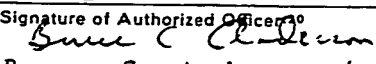


FIG. 7

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US87/01364

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC(4): H01J 40/00, 47/00; B05D 5/12 U.S. CL. 250/305, 307, 309, 310, 396R; 427/102; 313/363.1, 355		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
U.S.                    250/305, 307, 309, 310, 396R; 427/158, 102; 313/363.1		
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category <sup>6</sup>	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X	US,A, 4,587,425 (Plows) 06 May 1986, See entire document.	1-11, 13-18, 25
X	US,A, 4,551,599 (Liebl) 05 November 1985, See entire document.	1-11, 13-18, 25
X	US,A, 4,255,661 (Liebl) 10 March 1981, See entire document.	1-11, 13-18, 25
X	US,A, 3,845,305 (Liebl) 29 October 1974, See entire document.	1-11, 13-18, 25
A	US,A, 3,617,741 (Siegbahn et. al.) 02 November 1971.	1-11, 13-18, 25
A	US,A, 4,358,680 (Read) 09 November 1982.	1-11, 13-18, 25
X	US,A, 3,731,096 (Carter) 01 May 1973, See column 3, lines 44-47.	15, 16
X	US,A, 3,604,970 (Culbertson) 14 September 1971, See entire document.	15, 16
(cont.)		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>15</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>2</sup>		Date of Mailing of this International Search Report <sup>2</sup>
20 August 1987		22 SEP 1987
International Searching Authority <sup>1</sup>		Signature of Authorized Officer <sup>10</sup>
ISA/US		 Bruce C. Anderson/wb

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

X	US,A, 4,126,781 (Siegel) 21 November 1978, See Figs 4-5.	19-20 26-27
X	US,A, 4,255,656 (Barrie et. al.) 10 March 1981, See col. 3, third par..	19-20 26-27
X	US,A, 4,559,449 (Kesmodel) 17 December 1985, See entire document.	24, 28
X	US,A, 4,278,706 (Barry) 14 July 1981, See entire document.	21-23
X	US,A, 4,368,252 (Kakuashi et. al.) 11 January 1983, See entire document.	21-23

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>10</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers ..... because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:

2. ☐ Claim numbers ..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>11</sup>

This International Searching Authority found multiple inventions in this international application as follows:

(see attachment)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

telephone practice: claims 1-11 and 13-28

3. ☐ No required additional search fees were timely paid by the applicant. <sup>were searched</sup> Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.



PCT/US87/01364

I. Claims 1-11, 13-18, and 25 are, drawn to method and apparatus for extracting ions by applying a slowing diminishing field adjacent a supply, classified in Class 250, subclass 307.

II. Claims 21-23 are, drawn to product and method of coating, classified in Class 427, subclass 58.

III. Claim 12 is, drawn to a method of ionizing particles by autoionization, classified in Class 250, subclass 423P.

IV. Claims 19-20, 24 and 26-28 are, drawn to energy analyzer detectors having a resistive disk means and/or using two electrostatic spherical means with a telescope lens between, classified in Class 250, subclass 305.

